

# Accurate ionization potential of gold anionic clusters from density functional theory and many-body perturbation theory

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We present a theoretical study of the ionization potential in small anionic gold clusters, using density functional theory, with and without exact-exchange, and many body perturbation theory, namely the  $G_0W_0$  approach. We find that  $G_0W_0$  is the best approach and correctly describes the first ionization potential with an accuracy of about 0.1 eV.

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## INTRODUCTION

The peculiar properties exhibited by gold clusters made them a popular subject for physical chemistry studies and numerous applications in recent years, [1–8]. Unlike bulk gold, which is essentially chemically inert [9], gold clusters possess edge atoms that have a lower coordination and thus a higher reactivity. As a consequence, a close interplay between the structural and electronic properties of different Au nano-particles is observed and the determination of clusters sizes and shapes has a fundamental importance for both basic studies and applications.

Presently, the atomic structure of gold clusters can be established by a number of different experimental techniques [10] including photoelectron spectroscopy (PES) [11–18], ion mobility [19], infrared spectroscopy [20, 21], trapped ion electron diffraction [22–25], and photodissociation [26–28]. However, in all cases detailed information from theoretical investigations must complement the experimental data to allow the correct interpretation of the results and the final resolution of the different isomers. In this context, PES is a typical case, where photoelectron spectra obtained from theoretical calculations on a set of plausible structures are compared to the experimental peaks to assign the different features and identify the structure of the clusters.

Usually, the photoelectron spectrum of gold clusters is simulated by density functional theory (DFT) calculations, since these are easily affordable for a large variety of structures and provide direct access to approximate photoelectron spectra through the inspection of single-particle orbital energies (within the Kohn-Sham (KS) scheme [29]). However, generally the DFT calculations are performed using the generalized gradient approximation (GGA) for the exchange-correlation (XC) functional, and thus several drawbacks are introduced. The most important in the present context is the limitation regarding the description of the single-particle spec-

trum by these functionals. In fact, correct values of the orbital energies cannot be achieved in DFT when an approximate description of the exchange interaction is employed [30–32]. Due to the self-interaction error (SIE) [33, 34] present in GGA functionals, orbital energies are strongly overestimated and for a comparison with experimental data a rescaling of the energies is required based on additional calculations and/or experimental evidence [12, 35]. Alternatively, for an accurate estimation of the first ionization potential (IP),  $\Delta$ SCF calculations, based on total energy differences between the anionic and neutral species, can be considered [36].

More accurate orbital energies can be achieved with exact exchange (EXX) KS approaches, i.e. the optimized effective potential (OEP) method [37] or the localized Hartree-Fock (LHF) [30] approximation. A recent work showed in fact that accurate photoelectron spectra can be calculated for very small gold clusters (up to 4 atoms) by employing the LHF method together with a Lee-Yang-Paar (LYP) [38] correlation functional [39]. This approach is SIE-free and provides a good agreement with reference experimental data without the need for a rescaling of the orbital energies. It is thus potentially a valuable tool for the simulation of photoelectron spectra and the interpretation of PES experiments. However, despite the LHFLYP approach is much more accurate than conventional GGA methods, it has still two drawbacks: i) the correlation part of the functional is treated at the GGA level, and ii) it is yet a KS method, thus based on single-particle orbitals: even with the exact (unknown) XC functional the KS energy-level does not correspond to the exact PES levels [40], the only exception being the highest occupied molecular orbital (HOMO), which can be shown to be exactly related to the IP [40–42].

Alternative DFT approaches for the description of the PES levels are based on hybrid functionals, where a fraction of the non-local Hartree-Fock exchange is included in the Hamiltonian. This approach goes beyond the KS scheme and it is commonly applied for organic molecules. However, it has several problems when applied to metal-

lic systems, because of the drawbacks of the Hartree-Fock method in this case [43–45]. Therefore its use is essentially limited to small clusters. Moreover, hybrid approaches are mostly based on an error cancellation effects and thus can neither fully correct self-interaction error nor can provide systematic improvements, while they introduce several additional parameters. Reliable results can be obtained instead using range separated hybrid functionals [46], which take advantage of a screening of the Hartree-Fock exchange by separating short- and long-range effects.

The fundamental solution to probe PES experiments directly is to compute the quasiparticle energy spectrum [47, 48], as described by the quasiparticle equation

$$H_0(\mathbf{r})\phi_i^{QP}(\mathbf{r}) + \int d\mathbf{r}' \Sigma_{xc}(\mathbf{r}, \mathbf{r}', \epsilon_i^{QP})\phi_i^{QP}(\mathbf{r}') = \epsilon_i^{QP}\phi_i^{QP}(\mathbf{r}), \quad (1)$$

where  $H_0 = -(1/2)\nabla^2 + v_{ext} + V_H$  is the single-particle Hamiltonian,  $v_{ext}$  is the external (nuclear) potential,  $V_H$  is the Hartree potential and  $\Sigma_{xc}$  is the self-energy term: a non-local, non Hermitian and energy dependent operator resulting from all electron many-body interactions. Here  $\epsilon_i^{QP}$  and  $\phi_i^{QP}$  are the quasiparticle (QP) energies and eigenstates, respectively. Unfortunately, calculations of the exact self energy for real systems are computationally infeasible and approximations are required. We have calculated the self-energy operator within the GW approximation [49, 50].

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{2\pi} \int e^{i\omega'0^+} G(\mathbf{r}, \mathbf{r}', \omega - \omega') W(\mathbf{r}, \mathbf{r}', \omega') d\omega', \quad (2)$$

where  $G$  is the single particle Green's function and  $W$  is the dynamically screened Coulomb potential.

In principle, Eq. (2) requires a self-consistent solution [63, 64]. Nevertheless, for many systems the DFT wave functions are good approximations for the QP wavefunctions [30, 40, 48] and the quasiparticle energies  $\epsilon_n^{QP}$  can be obtained perturbatively ("one-shot" or  $G_0W_0$  calculations) from the starting one-electron energies  $\epsilon_n^0$  as:

$$\epsilon_n^{QP} = \epsilon_n^0 + \Re \langle \phi_n^0 | \Sigma(\epsilon_n^{QP}) - v_{xc} | \phi_n^0 \rangle. \quad (3)$$

Originally,  $G_0W_0$  has been applied in solids and, recently, calculations on bulk gold showed a QP band structure in good agreement with experimental PES [51]. Moreover, this approach has been used also for accurate calculations of the IP of finite-size systems, both in closed-shell [52–73] and open-shell [52, 74] species.

In this paper, we aim at assessing the merits and limitations of the different methods illustrated above and perform a comparative study of various computational approaches for the simulation of the first PES peak (i.e. IP) of several anionic gold clusters (up to 11 atoms; see fig. 1) for which experimental data are available.

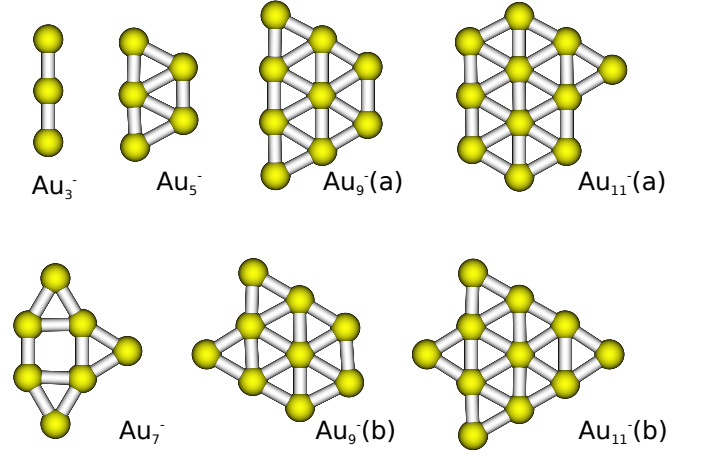


FIG. 1: Structures of gold cluster anions

## COMPUTATIONAL DETAILS

Reference IP energies and the general structure of the clusters were taken from Ref. [12]. Geometries were optimized using the PBEint XC functional [75], which has been shown to yield accurate results for such systems [76]. For the larger clusters ( $\text{Au}_7^-$ ,  $\text{Au}_9^-$  and  $\text{Au}_{11}^-$ ) we considered the lowest two structures from Ref. [12]. However, for  $\text{Au}_7^-$  at the PBEint/def2-TZVP level both isomers converged to the same geometry ( $\text{Au}_7^-$  A in Ref. [12]). This was also confirmed by TPSS/def2-QZVPP calculations [77, 78], which failed to identify a minimum-energy structure corresponding to  $\text{Au}_7^-$  B. Thus, only one structure for  $\text{Au}_7^-$  is considered here. The IP of different systems was obtained from the HOMO energy of the following methods: Hartree-Fock (HF), LHF [30], LH-FLYP [30, 38], PBEint [75], PBE0 [79]. In addition, we considered the  $\Delta$  SCF approach (PBEint functional) and the post-DFT many-body perturbation theory  $G_0W_0$  approach (from PBEint orbitals;  $G_0W_0@PBEint$ ). Finally, to assess the role of the reference orbitals for  $G_0W_0$  calculations we performed our perturbative treatment also starting from self-consistent static GW one-electron energy and orbital results ( $G_0W_0@COHSEX$ ), which have been recently shown to yield in solid-state physics similar results as the more computationally expensive self-consistent GW calculations [80, 81] and good agreement with the experimental transport properties of strongly correlated systems [64, 81, 82]. The COHSEX [80] is in fact a static version of the GW approximation, where the self-energy can be written as

$$\begin{aligned} \Sigma(\mathbf{r}, \mathbf{r}') = & - \sum_i^{occ} \phi_i^{QP}(\mathbf{r}) \phi_i^{QP}(\mathbf{r}') W(\mathbf{r}, \mathbf{r}', \omega = 0) \\ & + \frac{1}{2} \delta(\mathbf{r} - \mathbf{r}') (W(\mathbf{r}, \mathbf{r}', \omega = 0) - v(\mathbf{r} - \mathbf{r}')) \end{aligned} \quad (4)$$

i.e. as a sum of an instantaneous screened exchange (SEX) term and a Coulomb hole (COH) correlation term.

All DFT calculations were performed with the TURBOMOLE program package [83], using the def2-TZVP basis set [78] and a scalar relativistic effective core potential (ECP) replacing the inner 60 electrons of each gold atom [84]. The  $G_0W_0$  and the self-consistent COHSEX calculations were performed by using the FHI-AIMS program [85, 86] with the fourth-tier tight basis set (including additional  $f$ - and  $g$ -type functions) and scalar relativistic effects included through the zeroth-order relativistic approximation (ZORA) [87]. With this approach we estimate the  $G_0W_0$  orbital energies to be converged within 0.05 eV. Test calculations for the PBE0 and PBEint functionals showed that the results obtained by the two programs also differ by less than 0.05 eV. In GW calculations the self energy  $\Sigma$  was first calculated on the imaginary frequency  $\omega$ -grid and then analytically continued to the real axis grid as implemented in FHI-AIMS code [88].

## RESULTS AND DISCUSSION

The calculated IPs, as obtained with different methods, are listed in Tab. I, together with the experimental results. For  $Au_9^-$  and  $Au_{11}^-$  we report two isomers, because they are rather close in energy (at the PBEint level the (b) isomers are 0.21 and 0.07 eV higher for  $Au_9^-$  and  $Au_{11}^-$ , respectively). For  $Au_9^-$  (b) and  $Au_{11}^-$  COHSEX results are not present, because of the excessive computational cost. The last line of Tab. I reports the mean absolute error (MAE) with respect to experiment. This is calculated including all clusters but  $Au_9^-$  (b) and  $Au_{11}^-$  (a), because for these two clusters our best estimates ( $\Delta$ SCF and  $G_0W_0$ @PBEint) show that the IP is significantly lower than the experimental one, suggesting that these clusters are not measured in experiments.

The results confirm that the HOMO energy from GGA DFT calculations (PBEint results) is a very poor estimation of the IP, because the SIE leads to a strong underestimation of the orbital energies. Much better results are found instead when the Kohn-Sham calculations are performed using an effective exact-exchange approach, as the LHF one. In this case in fact the MAE drops to 0.66 eV and even further improvement can be achieved by inclusion of explicit correlation contributions (LHFLYP has a MAE of only 0.45 eV in line with the findings of Ref. [39]). We note, nonetheless, that this improvement is not systematic, as shown by the fact that LHFLYP performs well for the smaller clusters but it is worst than LHF for the largest ones. A possible reason for such a behavior traces back to the limitations of the semilocal LYP correlation potential [32] (similarly to other semilocal potentials). It is not fully compatible with exact-exchange or OEP approaches [89], and, more important, fails to

properly describe the correlation effects in extended systems of metallic character [90]. The net effect of the LYP functional is always to increase (in absolute value) the HOMO energy by approximately 0.7 eV, independently on the system under consideration. On the other hand,  $G_0W_0$  calculations suggest that the correlation effects are twice as big for the  $Au^-$  atom as for the largest clusters considered in this work, in agreement with the LHF vs. experimental trend.

The importance of correlation effects is also remarked by a comparison of the LHF results with the Hartree-Fock ones, as the latter display a larger overall MAE. The difference can be in fact attributed not only to the local KS approximation (full-OEP exact-exchange Kohn-Sham results are often closer to HF than LHF ones [30]), but also to the LHF approximations to the full OEP, which make effective correlation contributions appear in the KS potential, so that an effective partial screening of the exchange is obtained [39]. On the contrary, in the Hartree-Fock method the correlation is completely lacking (absence of any screening). Thus, Hartree-Fock calculations yield an overestimation of the electron-electron repulsion in metallic systems and the IP obtained through the HOMO energy is underestimated (for the same reason the  $s$ - $d$  splitting is overestimated in Hartree-Fock calculations on metallic systems [91]). This effect is instead mitigated in LHF calculations which in fact yield larger values for the IP. Finally, poor results are also obtained by considering the HOMO energy from hybrid calculations, as both GGA and HF results underestimate the reference experimental values, so that no benefit from error compensation can be obtained.

It is thus clear that to achieve a HOMO energy of high accuracy a proper treatment of exchange and correlation is necessary. This is indeed obtained within the  $G_0W_0$  (@PBEint) approach which in fact yields a MAE of only 0.14 eV, similarly with the  $\Delta$ SCF approach which is based on total energy differences (even slightly better  $G_0W_0$  results are found using PBE starting orbitals, with a MAE of 0.11 eV; note however that the difference is below the estimated accuracy for  $G_0W_0$  calculations). We remark that the  $\Delta$ SCF method can be only applied for the HOMO energy and few other orbital energies corresponding to the highest of each irreducible symmetry representation. On the contrary, the  $G_0W_0$  can be applied straightforwardly for the calculation of all the QP energies. We note however that the perturbative  $G_0W_0$  success in these calculations is not trivial: this method, originally applied to periodic systems, has quite few studies about molecules and clusters where the inhomogeneity of the density and low coordination number of atoms play an important role.

In this sense it is interesting to observe that for the present gold cluster  $G_0W_0$  calculations on top of self-consistent COHSEX (GW@COHSEX) show rather worse results than the GW@PBEint ones, in contrast to what

TABLE I: Ionization potential for several anionic gold clusters as resulting from different approaches: HF, LHF, LHFLYP, PBEint,  $\Delta$ SCF, PBE0, COHSEX,  $G_0W_0$ @COHSEX,  $G_0W_0$ @PBEint. Experimental data [12] are also reported. The last line shows the mean absolute error (MAE), excluding  $Au_9^-(b)$  and  $Au_{11}^-(a)$ . All results are in eV.

Cluster	HF	LHF	LHFLYP	PBEint	$\Delta$ SCF	PBE0	COHSEX	$G_0W_0$		Exp.
								@COHSEX	@PBEint	
Au $^-$	0.80	0.85	1.51	-0.84	2.09	-0.19	3.00	1.91	2.23	2.33
Au $_3^-$	2.46	2.88	3.57	1.20	3.57	1.82	4.84	3.69	3.92	3.88
Au $_5^-$	1.91	2.33	3.02	1.01	3.03	1.43	4.08	2.84	2.87	3.09
Au $_7^-$	2.15	2.43	3.14	1.59	3.39	1.89	4.45	3.25	3.30	3.46
Au $_9^-(a)$	2.89	3.55	4.28	1.95	3.71	2.45	4.98	3.75	3.57	3.83
Au $_9^-(b)$	2.36	2.83	3.56	1.73	3.44	2.09	-	-	3.30	(3.83)
Au $_{11}^-(a)$	2.69	3.23	3.96	2.03	3.65	2.39	-	-	3.52	(3.80)
Au $_{11}^-(b)$	3.05	3.77	4.50	2.18	3.81	2.62	-	-	3.73	3.80
MAE	1.19	0.76	0.45	2.22	0.14	1.73	0.95	0.23	0.14	

observed in solid-state calculations [81]. This is because of the poor quality of the COHSEX orbitals which overestimate quite significantly the reference ones. This behavior of the orbitals may trace back to the fact that in all clusters the HOMO is essentially described by a linear combination of  $s$  and  $p$  atomic orbitals, with negligible contribution from  $d$  and  $f$  atomic orbitals. In fact, scf-COHSEX was demonstrated to be a good starting point for  $G_0W_0$  when localized  $d$  and  $f$  orbitals [81] are important (e.g., in strongly correlated systems). However, it can be expected to yield a poor description of delocalized electrons as those lying in  $s$  and  $p$  orbitals, due to the lack of dynamical screening.

Finally, it is worthwhile to note that for the present case of gold anionic clusters the Hartree-Fock calculations always underestimate the reference IP, whereas the  $G_0W_0$  (and COHSEX) calculations yield an increase (in absolute value) of the HOMO energy with respect to HF. This behavior is opposite with respect to that usually observed in molecular systems where HF overestimates the IP due to the too negative value of the non-local exchange and GW has the effect of reducing the HOMO energy thanks to the screening of the exchange [63]. However, many exceptions exist, e.g. in atoms [52, 70], molecules [54] and metal clusters [62, 63, 73]. This latter behavior may be related to the important role of the correlation in systems such as the gold clusters studied here, which overtakes the screening. In fact, COHSEX calculations for the Au $^-$  atom show that the effect of the screening term is to shift-up the HOMO energy by 0.2 eV, whereas the Coulomb hole shifts it down by 2.1 eV. The anionic character of the clusters instead appears to play a negligible role, as similar findings are found also for neutral gold clusters [73].

## CONCLUSIONS

In conclusion, we have shown that refined many body calculations at the  $G_0W_0$ @PBEint level can describe the ionization potential of gold clusters with an accuracy of about 0.1 eV, outperforming any other orbital-based method. This result is a non-trivial confirmation of the goodness of the GW approach for metallic clusters and shows that the attainable accuracy is sufficient to distinguish between different isomeric forms of a cluster of a given size. Thus the  $G_0W_0$  approach can be used to select specific clusters geometries by comparison with experimental measurements (as in the case of Au $_9^-$  and Au $_{11}^-$ ). Similar results can be achieved at the  $\Delta$ SCF level, but losing any orbital picture. Finally, within the Kohn-Sham scheme, relatively accurate results can also be obtained when the effective exact exchange LHF method is employed (eventually in conjunction with a semilocal correlation functional). This approach has a considerably lower computational cost than the  $G_0W_0$  and thus may be considered as a cheaper alternative to the latter.

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